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SYNTHESIS OF A BRANCHED D-MANNOPENTAOSIDE AND A BRANCHED D-MANNOHEXAOSIDE: MODELS OF THE INNER CORE OF CELL-WALL GLYCOPROTEINS OF *Saccharomyces cerevisiae**

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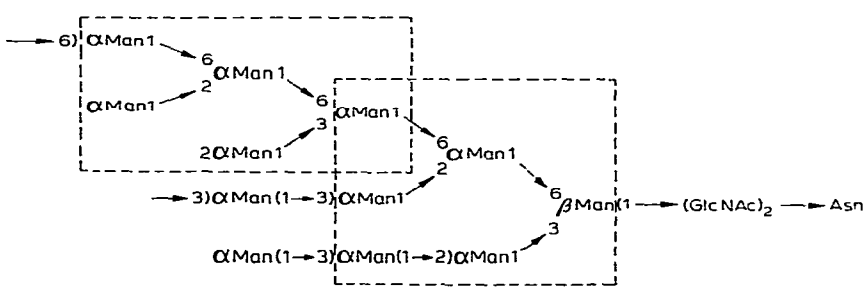
ABSTRACT

Synthetic routes are discussed to the branched D-mannopentaoside methyl 6-*O*-(2,6-di-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-3-*O*-α-D-mannopyranosyl-α-D-mannopyranoside and D-mannohexaoside methyl 6-*O*-(2,6-di-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-3-*O*-(2-*O*-α-D-mannopyranosyl-α-D-mannopyranosyl)-α-D-mannopyranoside, employing the properly benzylated D-mannobioside methyl 2,4-di-*O*-benzyl-6-*O*-(3,4-di-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside and D-mannotrioside methyl 2,4-di-*O*-benzyl-6-*O*-(3,4-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside as key intermediates.

INTRODUCTION

In 1974, Nakajima and Ballou[2] proposed that **1** is the inner-core structure of the D-mannan chain of *Saccharomyces cerevisiae* cell-wall glycoprotein, from the results of use of *mnn 2* mutant that makes, predominantly, an unbranched D-mannan outer chain attached to the inner core **1**.



1

*Synthetic Studies on Cell-surface Glycans, Part 7. For Part 6, see ref. 1.
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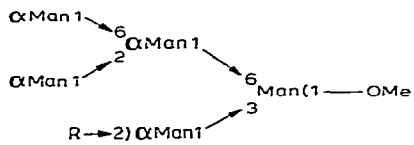
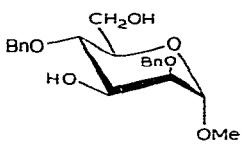
The proposed structure **1** may be regarded as being constructed from two blocks, **A** and **B** (indicated by the dotted lines in **1**). As the first step in experiments directed towards the reconstruction of such glycans as **1**, we chose for our synthetic targets two D-manno-oligosaccharides, **2** and **3**, which respectively correspond to block **A** and **B**, and we have now developed an efficient, synthetic sequence for both molecules.

The D-manno-oligosaccharides **2** and **3** may be retrosynthesized into three monosaccharide synthons already described, namely, one glycosyl acceptor[3,9] **4** and two glycosyl donors **5** (ref. 1; prepared[4] from **8**) and **6** (prepared[5] from **7**).



2 R = H
3 R = αMan(1→



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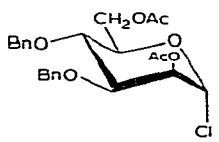

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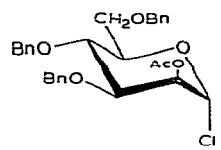

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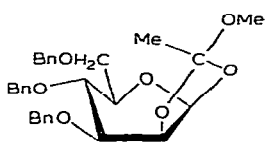
Bn = $PhCH_2$ Ac = CH_3CO



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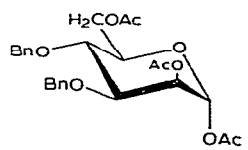

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RESULTS AND DISCUSSION

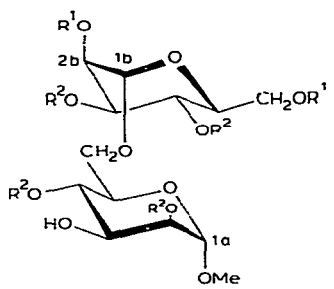
Synthesis of the key intermediates **10** *and* **14**

The partially benzylated D-mannobioside **10** was synthesized *via* selective glycosylation of the primary OH group of diol **4** with 1.25 molar equivalents of the glycosyl donor **5** according to the Hanessian–Banoub procedure[6], which led to the isolation of the protected D-mannobioside **9** in 40% yield. The ^{1}H-n.m.r. spectrum of **9** showed two singlets for two acetyl groups, at δ 1.98 and 2.13, and a deshielded triplet for H-2b at δ 5.44 (J 2 Hz). In the ^{13}C-n.m.r. spectrum were observed signals with $^1J_{CH}$ ~170 Hz, for two anomeric carbon atoms (C-1a and C-1b) having the α-D configuration, at δ 97.6 and 97.8, in agreement with the empirical rule of Bock and Pedersen[7]. Zemplén deacetylation of **9** gave a 92.3% yield of **10**, which is suitable

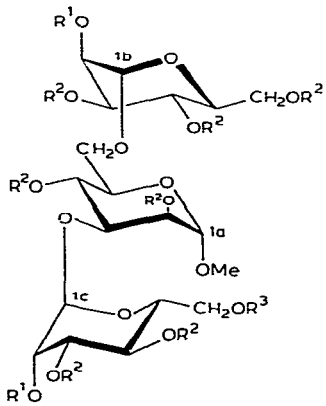
for further glycosylation. Catalytic hydrogenolysis of **10** over 10% Pd–C in aq. EtOH afforded an amorphous, free D-mannobioside **11**, which was identical with an authentic sample[8], thus establishing the (1→6) nature of the interglycosidic linkage in **10**.

Another key intermediate, namely, **14**, could readily be derived from the protected D-mannobioside **9**. Glycosylation[6] of **9** with 2 molar equivalents of glycosyl donor **6** led to the isolation of the protected D-mannotrioside **13** in 82.2% yield. The structure of **13** was confirmed as follows. The ^{1}H-n.m.r. spectrum showed three singlets, for three acetyl groups, at δ 1.97, 2.06, and 2.13, and the ^{13}C-n.m.r. spectrum contained two signals, with $^1J_{CH}$ ~170 Hz, for three anomeric carbon atoms having the α-D configuration, at δ 97.8 and 98.0 for C-1a and C-1b, and at δ 99.5 for C-1c. Zemplén deacetylation of **13** gave rise to the partially benzylated D-mannotrioside **14** in 87.2% yield; its ^{13}C-n.m.r. spectrum contained three signals, with $^1J_{CH}$ ~170 Hz, at δ 98.5 (C-1a), 99.6 (C-1b), and 101.5 (C-1c). The structure of **14** was further confirmed by its conversion into free D-mannotrioside **15**, which was identical with an authentic sample[9].

The two key intermediates, **10** and **14**, having been prepared unambiguously, further glycosylation toward the target molecules **2** and **3** was next examined.



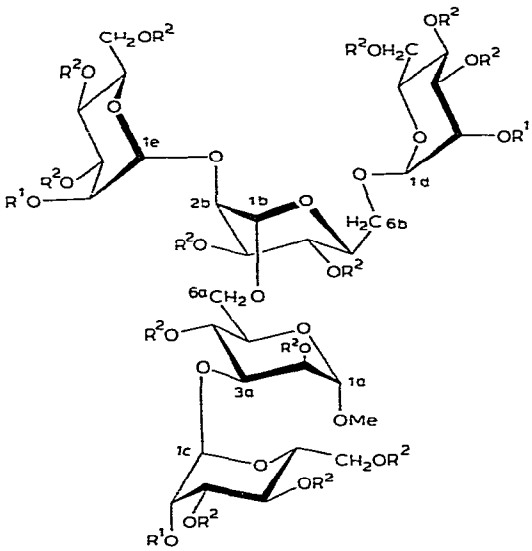
9 R^1 = Ac, R^2 = Bn
10 R^1 = H, R^2 = Bn
11 R^1 = R^2 = H



12 R^1 = R^3 = Ac, R^2 = Bn
13 R^1 = Ac, R^2 = R^3 = Bn
14 R^1 = H, R^2 = R^3 = Bn
15 R^1 = R^2 = R^3 = H

Synthesis of the branched D-*mannopentaoside* **2** *and* D-*mannohexaoside* **3**

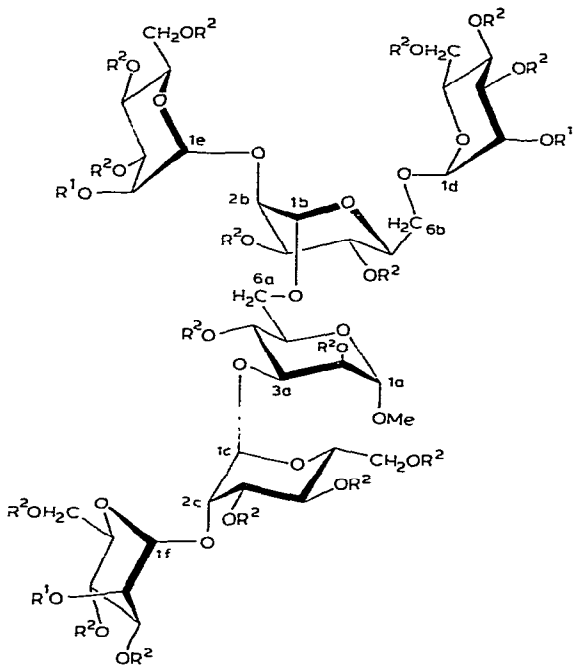
Glycosylation[6] of triol **10** with 5.8 molar equivalents of glycosyl donor **6** gave rise to the protected mannopentaoside **16** in 74.8% yield. The structure of **16** was confirmed by the ^{1}H- and ^{13}C-n.m.r. data, which showed three singlets, for three acetyl groups, at δ 2.07, 2.09, and 2.14, and four signals, with $^1J_{CH}$ ~170 Hz, for five anomeric carbon atoms having the α-D configuration, at δ 97.2 (C-1d), 97.9 (C-1a),



16 R^1 = Ac, R^2 = Bn
17 R^1 = H, R^2 = Bn
2 R^1 = R^2 = H

98.8 (C-1b), and 99.4 (C-1c and C-1e). Zemplén deacetylation of **16** to **17**, and catalytic hydrogenolysis of **17**, led to isolation of the free D-mannopentaoside **2**. The structure of **2** was deduced from the synthetic sequence that used the regiospecifically benzylated D-mannobioside **10** as the key intermediate, and was confirmed by the ^{1}H- and ^{13}C-n.m.r. data. The ^{1}H-n.m.r. spectrum contained four doublets, with J 2 Hz, for five anomeric protons, at δ 4.70 (H-1a), 4.89 (H-1d), 5.01 (H-1e), and 5.08 (H-1b and H-1c), and the ^{13}C-n.m.r. spectrum showed four signals, with $^1J_{CH}$ ~170 Hz, for five anomeric carbon atoms having the α-D configuration, at δ 98.2 (C-1b), 99.7 (C-1d), 101.3 (C-1a), and 102.7 (C-1c and C-1e), and two deshielded signals, due to the glycosidation shift[10], at δ 65.9 (for C-6a and C-6b) and δ 79.0 (for C-2b and C-3a), confirming both the stereochemistry of the glycosylation and the regiochemistry of the chain branching.

The key intermediate **14** could be transformed into the target D-mannan **3** in a similar way. Thus, glycosylation of triol **14** with 5.6 molar equivalents of glycosyl donor **6** afforded an 85.9% yield of protected mannohexaoside **18**, the ^{13}C-n.m.r. spectrum of which contained six signals, with $^1J_{CH}$ ~170 Hz, for six anomeric carbon atoms having the α-D configuration, at δ 97.5 (C-1d), 97.9 (C-1a), 99.0 (C-1b), 99.4 (C-1f), 99.6 (C-1e), and 100.9 (C-1c). Zemplén deacetylation of **18** to **19**, and catalytic hydrogenolysis of **19**, gave rise to the target molecule, the free D-mannohexaoside **3**, as an amorphous powder. The structure of **3** was deduced from the synthetic sequence, and was confirmed by the following ^{1}H- and ^{13}C-n.m.r. data. The ^{1}H-n.m.r. spectrum showed six doublets, with J 2 Hz, for six anomeric protons,



18 R^1 = Ac, R^2 = Bn
19 R^1 = H, R^2 = Bn
3 R^1 = R^2 = H

at δ 4.70 (H-1a), 4.90 (H-1d), 5.01 (H-1f), 5.03 (H-1e), 5.08 (H-1b), and 5.28 (H-1c). The ^{13}C-n.m.r. data revealed five signals, with $^1J_{CH}$ ~170 Hz, for six anomeric carbon atoms having the α-D configuration, at δ 98.2 (C-1b), 99.7 (C-1d), 101.2 (C-1c), 101.3 (C-1a), and 102.6 (C-1e and C-1f), and four deshielded signals, due to the glycosidation shift[10], at δ 65.6 and 65.9 (for C-6a and C-6b), and δ 78.6 (2 C) and 79.1 (1 C) (for C-2b, C-2c, and C-3a).

In conclusion, the branched D-mannopentaoside **2** and D-mannohexaoside **3** were synthesized by unambiguous routes employing the partially benzylated D-mannobioside **10** and D-mannotrioside **14** as key intermediates. It may be noted that the partially benzylated D-mannopentaoside **17** and D-mannohexaoside **19** may constitute important glycosyl acceptors for the synthesis of higher D-manno-oligosaccharide chains.

EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 141 polarimeter, for solutions in $CHCl_3$ at 25°, unless otherwise noted. Column chromatography was performed on columns of Silica Gel Merck

(70–230 mesh; E. Merck, Darmstadt, Germany). Thin-layer chromatography (t.l.c.) was performed on precoated plates (layer thickness, 0.25 mm) of Silica Gel 60 F_{254} (E. Merck, Darmstadt, Germany). I.r. spectra were recorded with an EPI-G2 Hitachi Spectrophotometer, using KBr pellets for the crystalline samples, and neat films for the liquid samples. ^{1}H-N.m.r. spectra were recorded with a Varian HA-100 n.m.r. spectrometer, using tetramethylsilane as the internal standard. ^{13}C-N.m.r. spectra were recorded with a JNM-FX 100FT n.m.r. spectrometer operated at 25.05 MHz. The values of δ_C and δ_H are expressed in p.p.m. downwards from the internal standard, for solutions in $CDCl_3$, unless otherwise noted.

*Methyl 2,4-di-*O*-benzyl-6-*O*-(2,6-di-*O*-acetyl-3,4-di-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**9**). — A mixture of **4** (1.873 g, 5.0 mmol) and $AgSO_3CF_3$ (2.4 g, 9.3 mmol) was dried *in vacuo* for 3 h at 20°. To this mixture were added $Me_2NCONMe_2$ (2.6 mL, 21.7 mmol), CH_2Cl_2 (8 mL), and half of a solution of **5** [3.09 g: prepared[4] from **8** (3.05 g, 6.25 mmol)] in CH_2Cl_2 (7 mL) at −10 to −15° with stirring, under argon. After the mixture had been stirred for 3 h at 20°, the rest of the solution of **5** in CH_2Cl_2 was added, and the mixture was stirred for 4 days at 20° under argon, diluted with CH_2Cl_2 (50 mL), and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$, dried ($MgSO_4$), and evaporated *in vacuo*, to afford an oily residue (6.27 g) which was chromatographed on SiO_2 (500 g) with 40:1 CH_2Cl_2–Me_2CO, to give **9** (1.628 g, 39.8%)*, $[\alpha]_D$ +49.0° (*c* 0.30); R_F 0.41 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 1.98 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 3.27 (s, 3 H, OMe), 5.44 (bt, 1 H, *J* 2 Hz, H-2b); δ_C: 20.8 (Ac), 21.0 (Ac), 54.7 (OMe), 66.0 (C-6a), 71.3 (O-3-CH_2Ph), 72.9 (O-2-CH_2Ph), 74.6 and 75.1 (2 O-4-CH_2Ph), and 97.6 and 97.8 ($^1J_{CH}$ 170.6 Hz, C-1a, 1b).

Anal. Calc. for $C_{45}H_{52}O_{13}$: C, 67.48; H, 6.55. Found: C, 66.25; H, 6.41.

*Methyl 2,4-di-*O*-benzyl-6-*O*-(3,4-di-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**10**). — A solution of **9** (694 mg, 0.87 mmol) in MeOH (20 mL) and 2M NaOMe–MeOH (0.2 mL) was stirred for 16 h at 20°, and then made neutral with Amberlist 15 (H^+) resin. The resin was filtered off through Celite, and the filtrate was evaporated *in vacuo*, to give an amorphous residue (627 mg) which was chromatographed on SiO_2 (50 mg) with 15:1 CH_2Cl_2–Me_2CO, to give **10** (619.5 mg, 92.3%), $[\alpha]_D$ +58.8° (*c* 0.40); R_F 0.11 in 20:1 CH_2Cl_2–Me_2CO; δ_H: 3.26 (s, 3 H, OMe), 4.92 (d, 1 H, *J* 2 Hz, H-1a), and 5.00 (d, 1 H, *J* 2 Hz, H-1b); δ_C: 54.8 (OMe), 66.2 (C-6a), 71.6 (O-3-CH_2Ph), 72.9 (O-2-CH_2Ph), 74.6 and 75.0 (2 O-4-CH_2Ph), 97.7 ($^1J_{CH}$ 166.2 Hz, C-1a), and 99.4 ($^1J_{CH}$ 169.1 Hz, C-1b).

Anal. Calc. for $C_{41}H_{48}O_{11} \cdot H_2O$: C, 67.01; H, 6.96. Found: C, 67.05; H, 6.65.

*Methyl 6-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**11**). — A mixture of **10** (56 mg, 76 μmol) and 10% Pd–C (50 mg) in EtOH (10 mL) and H_2O (1 mL) was stirred under H_2 for 4 h at 45–50°, filtered through Celite, and evaporated *in*

*An appreciable amount of product **9** seemed to be adsorbed on the silica-gel column in this particular case, for as-yet-unknown reasons.

vacuo, to afford **11** (26.9 mg, 96.2%) as an amorphous, hygroscopic powder whose ^{1}H- and ^{13}C-n.m.r. data were identical with those of an authentic sample[8].

Methyl 3-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4-di-O-benzyl-6-O-(2,6-di-O-acetyl-3,4-di-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**13**). — To a mixture of **9** (800 mg, 0.98 mmol) and $AgSO_3CF_3$ (790 mg, 3.07 mmol), dried *in vacuo* for 3 h, were added CH_2Cl_2 (5 mL), $Me_2NCONMe_2$ (0.85 mL, 7.1 mmol), and half of a solution of **6** [1.07 g; prepared[5] from **7** (1.02 g, 2.0 mmol)] in CH_2Cl_2 (5 mL) at −10 to −15° with stirring, under argon. After stirring for 3.5 h at 20°, the rest of the solution of **6** in CH_2Cl_2 was added at −10 to −15°, and the mixture was stirred for 16 h at 20°. The usual processing gave an oily residue (2.34 g) which was chromatographed on SiO_2 (200 g) with 3:1 toluene–EtOAc, to afford **13** (1.014 g, 82.2%), $[\alpha]_D$ +43.2° (*c* 0.53); R_F 0.34 in 3:1 toluene–EtOAc; δ_H: 1.97, 2.06, and 2.13 (3 s, 9 H, 3 Ac), 3.21 (OMe), 4.81, 4.91, and 5.17 (3 bs, 3 H, 3 H-1), 5.46 (bt, 2 H, J ~2 Hz, H-2b, 2c); δ_C: 20.8 and 21.0 (2 OAc), 54.8 (OMe), 63.3 (C-6b), 66.5 (C-6a), 69.2 (C-6c), 71.3 and 71.8 (2 O-3-CH_2Ph), 72.3 (O-2-CH_2Ph), 73.4 (O-6-CH_2Ph), 75.0 (3 O-4-CH_2Ph), 77.3 (C-3a), 97.8 and 98.0 ($^1J_{CH}$ 172 Hz, C-1a, 1b), and 99.5 ($^1J_{CH}$ 172.0 Hz, C-1c).

Anal. Calc. for $C_{74}H_{82}O_{19} \cdot H_2O$: C, 68.71; H, 6.54. Found: C, 68.64; H, 6.52.

Methyl 2,4-di-O-benzyl-6-O-(3,4-di-O-benzyl-α-D-mannopyranosyl)-3-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**14**). — A solution of **13** (885.5 mg, 685 μmol) in MeOH (25 mL)–THF (10 mL) and 2M NaOMe–MeOH (0.3 mL) was stirred for 16 h at 20°. The usual processing gave a residue (763 mg) which was chromatographed on SiO_2 (75 g) with 10:1 CH_2Cl_2–Me_2CO, to afford **14** (702 mg, 87.2%), $[\alpha]_D$ +45.2° (*c* 0.29); R_F 0.16 in 10:1 CH_2Cl_2–Me_2CO: δ_H: 3.23 (s, 3 H, OMe), 5.03 (bs, 1 H, H-1b), and 5.22 (bs, 1 H, H-1c); δ_C: 54.8 (OMe), 61.8 (C-6b), 66.1 (C-6a), 69.3 (C-6c), 71.8 and 72.0 (2 O-3-CH_2Ph), 72.3 (O-2-CH_2Ph), 73.5 (O-6-CH_2Ph), 74.9 (3 O-4-CH_2Ph), 77.6 (C-3a), 98.5 ($^1J_{CH}$ 166.2 Hz, C-1a), 99.6 ($^1J_{CH}$ 170.6 Hz, C-1b), and 101.5 ($^1J_{CH}$ 172.1 Hz, C-1c).

Anal. Calc. for $C_{68}H_{76}O_{16} \cdot 1.5\ H_2O$: C, 69.43; H, 6.77. Found: C, 69.31; H, 6.57.

Methyl 3,6-di-O-α-D-mannopyranosyl-α-D-mannopyranoside (**15**). — A mixture of **14** (54 mg, 46 μmol) and 10% Pd–C (40 mg) in EtOH (10 mL) and H_2O (1 mL) was stirred under H_2 for 4.5 h at 50°. The usual processing afforded amorphous, powdery **15** (24 mg, quantitative), $[\alpha]_D$ +83.9° (*c* 0.18, H_2O); R_F 0.37 in 2:1:1 1-BuOH–EtOH–H_2O. The ^{1}H-n.m.r. data (in D_2O at 60°) were identical with those of an authentic sample[9].

Methyl 3-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-2,4-di-O-benzyl-6-O-[2,6-di-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-3,4-di-O-benzyl-α-D-mannopyranosyl]-α-D-mannopyranoside (**16**). — Triol **10** was co-evaporated several times with dry CH_2Cl_2, and dried *in vacuo* for 16 h. A mixture of **10** (490 mg, 0.68 mmol) and $AgSO_3CF_3$ (1.52 g, 5.9 mmol) was dried *in vacuo* for 4 h at 20°. To this mixture were added CH_2Cl_2 (5 mL), $Me_2NCONMe_2$ (1.0 mL, 8.3 mmol), and half of a solution of **6** [2.096 g, prepared[5] from **7** (2.00 g, 3.95 mmol)] in CH_2Cl_2

(6 mL) at −10 to −15° with stirring, under argon. After the mixture had been stirred for 4 h at 20°, the rest of the solution of **6** in CH_2Cl_2 was added, and the mixture was stirred for 1 day. The usual processing gave an oily product (3.07 8g) which was chromatographed on SiO_2 (250 g) with 11:1 toluene–THF, to give a fraction (1.7 g) containing **16** as the major product. Re-chromatography of this fraction on SiO_2 (300 g) with 19:1 toluene–THF gave **16** (1.095 g, 74.8%), $[\alpha]_D$ +40.3° (*c* 0.35); R_F 0.37 in 10:1 toluene–THF; δ_H: 2.07, 2.09, and 2.14 (3 s, 9 H, 3 OAc), and 3.18 (s, 3 H, OMe); δ_C: 21.0 (3 OAc), 54.6 (OMe), 97.2 ($^1J_{CH}$ 172.1 Hz, C-1d), 97.9 ($^1J_{CH}$ 167.7 Hz, C-1a), 98.8 ($^1J_{CH}$ 172.1 Hz, C-1b), and 99.4 ($^1J_{CH}$ 172.1 Hz, C-1c, 1e).

Anal. Calc. for $C_{128}H_{138}O_{29}$: C, 71.82; H, 6.50. Found: C, 71.76; H, 6.51.

*Methyl 2,4-di-*O*-benzyl-6-*O*[3,4-di-*O*-benzyl-2,6-di-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranosyl]-3-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**17**). — A solution of **16** (972 mg, 0.45 mmol) in MeOH (25 mL)–THF (10 mL) and 2M NaOMe–MeOH (0.2 mL) was stirred for 16 h at 20°. The usual processing gave crude **17** (945 mg) containing traces of impurities. Chromatography on SiO_2 (90 g) with 30:1 CH_2Cl_2–THF afforded pure **17** (715.5 mg, 78.3%), $[\alpha]_D$ +60.0° (*c* 0.13); R_F 0.21 in 30:1 CH_2Cl_2–THF; δ_H: 3.17 (s, 3 H, OMe), 5.18 (bs, 1 H, H-1), and 5.04 (bs, 2 H, 2 H-1); δ_C: 54.6 (OMe), 98.2 ($^1J_{CH}$ 166.2 Hz, C-1a), 98.8 ($^1J_{CH}$ 172.1 Hz, C-1b), 99.6 ($^1J_{CH}$ 172.1 Hz, C-1d), and 101.3 ($^1J_{CH}$ 169.1 Hz, C-1c, 1e).

Anal. Calc. for $C_{122}H_{132}O_{26}$: C, 72.74; H, 6.61. Found: C, 72.70; H, 6.75.

*Methyl 6-*O*-(2,6-di-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranosyl)-3-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**2**). — A mixture of **17** (364.5 mg, 0.18 mmol) and 10% Pd–C (200 mg) in EtOH (30 mL) and H_2O (6 mL) was stirred under H_2 for 8 h at 50°. The usual processing gave **2** (152 mg, 98.1%) as an amorphous powder, $[\alpha]_D$ +91.7° (*c* 0.42, H_2O); R_F 0.18 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O at 60°): 3.40 (s, 3 H, OMe), 4.70 (d, 1 H, *J* 2 Hz, H-1a), 4.89 (d, 1 H, *J* 2 Hz, H-1d), 5.01 (d, 1 H, *J* 2 Hz, H-1e), and 5.08 (d, 2 H, *J* 2 Hz, H-1b, 1c); δ_C (D_2O): 55.2 (OMe), 65.4 and 65.9 (C-6a, 6b), 79.0 (C-2b, 3a), 98.2 ($^1J_{CH}$ 171.9 Hz, C-1b), 99.7 ($^1J_{CH}$ 171.9 Hz, C-1d), 101.3 ($^1J_{CH}$ 169.9 Hz, C-1a), and 102.7 ($^1J_{CH}$ 171.9 Hz, C-1c, 1e).

Anal. Calc. for $C_{31}H_{54}O_{26} \cdot H_2O$: C, 43.25; H, 6.56. Found: C, 43.27; H, 6.70.

*Methyl 3-*O*-[2-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl]-2,4-di-*O*-benzyl-6-*O*-[2,6-di-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-3,4-di-*O*-benzyl-α-*D*-mannopyranosyl]-α-*D*-mannopyranoside* (**18**). — Triol **14** was coevaporated several times with CH_2Cl_2, and dried *in vacuo* for 16 h at 20°. A mixture of this dried **14** (590 mg, 0.5 mmol) and $AgSO_3CF_3$ (1.1 g, 4.3 mmol) was dried *in vacuo* for 3 h at 20°. To this mixture were added CH_2Cl_2 (5 mL), $Me_2NCONMe_2$ (0.65 mL, 5.4 mmol), and half of a solution of **6** [1.55 g, prepared from **7** (1.43 g, 2.8 mmol)] in CH_2Cl_2 (5 mL) at −10 to −15° with stirring, under argon. After stirring the mixture for 18 h at 20°, the remaining solution of **6** in CH_2Cl_2 was added at −10 to −15°, and the mixture was stirred for 19 h at 20° under argon. The usual processing gave an oily product (2.388 g) which

was chromatographed on SiO_2 (200 g) with 19:1 toluene–THF, to give **18** (1.110 g, 85.9%), $[\alpha]_D$ +41.6° (*c* 0.56); R_F 0.38 in 10:1 toluene–THF; δ_H: 2.03 (s, 3 H, OAc), 2.09 (s, 6 H, 2 OAc), and 3.14 (s, 3 H, OMe); δ_C: 21.1 (3 OAc, 54.7 (OMe), 97.5 ($^1J_{CH}$ 172.1 Hz, C-1d), 97.9 ($^1J_{CH}$ 172.1 Hz, C-1a), 99.0 ($^1J_{CH}$ ~170 Hz, C-1b), 99.4 ($^1J_{CH}$ ~170 Hz, C-1f), 99.6 ($^1J_{CH}$ ~170 Hz, C-1e), and 100.9 ($^1J_{CH}$ 173.5 Hz, C-1c).

Anal. Calc. for $C_{155}H_{166}O_{34}$: C, 72.35; H, 6.50. Found: C, 71.97; H, 6.55.

*Methyl 2,4-di-*O*-benzyl-6-*O*-[3,4-di-*O*-benzyl-2,6-di-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranosyl]-3-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(3,4,6-tri-*O*-benzyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranosyl]-α-*D*-mannopyranoside* (**19**). — A solution of **18** (957 mg, 0.37 mmol) in MeOH (45 mL)–THF (15 mL) and 2M NaOMe–MeOH (0.2 mL) was stirred for 16 h at 20°. The usual processing, and chromatography on SiO_2 (80 g) with 20:1 CH_2Cl_2–Me_2CO afforded **19** (695 mg, 75.8%), $[\alpha]_D$ +56.7° (*c* 0.275); R_F 0.24 in 20:1 CH_2Cl_2–Me_2CO: δ_H: 3.16 (s, 3 H, OMe), 5.04 (4 H-1), and 5.24 (H-1); δ_C: 54.5 (OMe), 97.7 ($^1J_{CH}$ 167.0 Hz, C-1a), 98.5 ($^1J_{CH}$ 170.9 Hz, C-1b), 99.4 ($^1J_{CH}$ 170.9 Hz, C-1d), 100.8 ($^1J_{CH}$ 171.9 Hz, C-1c, 1f), and 101.2 ($^1J_{CH}$ 168.9 Hz, C-1e).

Anal. Calc. for $C_{149}H_{160}O_{31} \cdot H_2O$: C, 72.60; H, 6.63. Found: C, 72.63; H, 6.59.

*Methyl 6-*O*-(2,6-di-*O*-mannopyranosyl-α-*D*-mannopyranosyl)-3-*O*-(2-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**3**). — A mixture of **19** (300 mg, 0.12 mmol) and 10% Pd–C (200 mg) in EtOH (30 mL) and H_2O (4 mL) was stirred under H_2 for 7.5 h at 50°. The usual processing afforded **3** (130.7 mg, quantitative) as an amorphous material, $[\alpha]_D$ +79.4° (*c* 0.53, H_2O); R_F 0.14 in 2:1:1 1-BuOH–EtOH–H_2O; δ_H (D_2O, 60°): 3.38 (s, 3 H, OMe), 4.70 (d, 1 H, *J* 2 Hz, H-1a), 4.90 (d, 1 H, *J* 2 H, H-1d), 5.01 (d, 1 H, *J* 2 Hz, H-1f), 5.03 (d, 1 H, *J* 2 Hz, H-1e), 5.08 (d, 1 H, *J* 2 Hz, H-1b), and 5.28 (d, 1 H, *J* 2 Hz, H-1c): δ_C (D_2O): 55.2 (OMe), 65.6 and 65.9 (C-6a, 6b), 78.6 and 79.1 (2:1, C-2b, 2c, 3a), 98.2 ($^1J_{CH}$ 171.9 Hz, C-1b), 99.7 ($^1J_{CH}$ 170.9 Hz, C-1d), 101.2 ($^1J_{CH}$ 172.9 Hz, C-1c), 101.3 ($^1J_{CH}$ 172.9 Hz, C-1a), and 102.6 ($^1J_{CH}$ 170.9 Hz, C-1e, 1f).

Anal. Calc. for $C_{37}H_{64}O_{31} \cdot 3\ H_2O$: C, 41.96; H, 6.66. Found: C, 42.02; H, 6.38.

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REFERENCES

1 T. Ogawa and K. Sasajima, *Carbohydr. Res.*, 93 (1981) 67–81.
2 T. Nakajima and C. E. Ballou, *J. Biol. Chem.*, 249 (1974) 7685–7694.
3 T. Ogawa and M. Matsui, *Carbohydr. Res.*, 62 (1978) c1–c4.

4 M. M. PONPIPOM, *Carbohydr. Res.*, 59 (1977) 311–317.
5 T. OGAWA, K. KATANO, AND M. MATSUI, *Carbohydr. Res.*, 64 (1978) c3–c9.
6 S. HANESSIAN AND J. BANOUB, *Carbohydr. Res.*, 53 (1977) c13–c16; *ACS Symp. Ser.*, 39 (1976) 36–63.
7 K. BOCK, I. LUNDT, AND C. PEDERSEN, *Tetrahedron Lett.*, (1973) 1037–1040; K. BOCK AND C. PEDERSEN, *J. Chem. Soc., Perkin Trans. 2*, (1974) 293–297; *Acta Chem. Scand. Ser. B*, 29 (1975) 258–264.
8 T. OGAWA AND K. SASAJIMA, *Tetrahedron*, in press.
9 T. OGAWA, K. KATANO, K. SASAJIMA, AND M. MATSUI, *Tetrahedron*, in press.
10 L. RADICS, M. KAJTAR-PEREDY, S. CORSANO, AND L. STANDOLI, *Tetrahedron Lett.*, (1975) 4287–4290; K. TORI, T. HIRATA, O. KOSHITANI, AND T. SUGA, *ibid.*, (1976) 1311–1314; K. YAMASAKI, H. KOHDA, T. KOBAYASHI, R. KASAI, AND O. TANAKA, *ibid.*, (1976) 1005–1008; K. TORI, S. SEO, Y. YOSHIMURA, M. NAKAMURA, Y. TOMITA, AND H. ISHII, *ibid.*, (1976) 4167–4170.